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This report describes a contribution of the U.S Geological Survey to the Clinch River Study.  Radioactive waste from ORNL have been released to White Oak Creek, which enters the Clinch river 20.8 miles upstream from the junction with the Tennessee river.  Samples of water from the three streams were taken one-or more times daily at seven sampling stations during a period of 3 years and composited into weekly or monthly samples according to stream flow.  Determinations were made of physical parameters of the content of stable chemical constituents, radiochemical constituents, and suspended sediment in the composite sample.  This paper presents and summarizes the results.

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# Composition of Water in Clinch River, Tennessee River, And Whiteoak Creek as Related to Disposal of Low-Level Radioactive Liquid Wastes

GEOLOGICAL SURVEY PROFESSIONAL PAPER 433-J

# Composition of Water in Clinch River, Tennessee River, And Whiteoak Creek as Related to Disposal of Low-Level Radioactive Liquid Wastes

*By* R. J. PICKERING

TRANSPORT OF RADIONUCLIDES BY STREAMS

GEOLOGICAL SURVEY PROFESSIONAL PAPER 433-J

# CONTENTS

# ILLUSTRATIONS

# TABLES

III

# COMPOSITION OF WATER IN CLINCH RIVER, TENNESSEE RIVER, AND WHITEOAK CREEK AS RELATED TO DISPOSAL OF LOW-LEVEL RADIOACTIVE LIQUID WASTES

By R. J. PICKERING

## ABSTRACT

Low-level-radioactive wastes have been released to the Clinch River from the Oak Ridge National Laboratory in eastern Tennessee since 1943, when the Laboratory first began processing radioactive materials. The fate of the radioactive wastes and the mechanisms by which the contained radionuclides are dispersed in the river have been investigated as part of the Clinch River Study, a multiagency effort to evaluate the present and future use of the river for the disposal of such wastes. As one element of the study, the composition of water in the streams which receive the radioactive wastes has been characterized through an intensive program of water sampling.

Radioactive wastes from the Laboratory are released to Whiteoak Creek, which enters the Clinch River 20.8 miles upstream from where the Clinch River joins the Tennessee River. Samples of water from the three streams were taken one or more times daily at seven sampling stations during a period of 3 years and composited into weekly or monthly samples according to streamflow. Determinations were made of physical parameters and of the content of stable chemical constituents, radiochemical constituents, and suspended sediment in the composite samples.

Results of the analyses showed that all three streams contain water of the calcium bicarbonate type, presumably as a result of the abundance of limestone and dolomite bedrock underlying their drainage basins. Tennessee River water is similar in composition to Clinch River water, but contains somewhat less bicarbonate, calcium, magnesium, and suspended and dissolved solids, and somewhat more sodium and chloride. Whiteoak Creek water is more highly mineralized than the other two streams, and has a higher average content of sulfate, nitrate, phosphorus, and sodium.

Turbidity, apparent color, centrifuged color, and suspended solids, all largely controlled by seasonal variations in rainfall and runoff, varied with time in the same general manner in both the Clinch River and the Tennessee River. Hardness, calcium, magnesium, sodium, and chloride showed maximum concentrations in the autumn, when contribution of ground water to streamflow is greatest and dilution of wastes is least. Iron and manganese varied in the same manner as suspended solids in both rivers. This variation suggests that those constituents were present in the water primarily in association with solid particles.

Most of the cesium-137 entering the Clinch River in Whiteoak Creek water was associated with suspended solids having a diameter larger than that of colloidal particles. This association persisted in the lower Clinch River, but in the Tennessee River, cesium-137 was either dissolved in the water or associated with solids of colloidal or near-colloidal size.

Comparisons of variations in radionuclide content with variations in stable chemical content of water samples indicated that much of the strontium-90 present in Whiteoak Creek water may have been associated with precipitated calcium carbonate. Close similarities in variations in concentration between ruthenium-106 and cobalt-60 in both Whiteoak Creek and the Clinch River, and correlation of the two radionuclides with nitrate at Whiteoak Dam, reflected their common origin in high-nitrate solutions released to the basin of Whiteoak Creek. Their lack of correlation with cesium-137 and strontium-90 indicated other origins for those radionuclides.

## INTRODUCTION

Since 1943, when the Oak Ridge National Laboratory (ORNL) in eastern Tennessee first began processing radioactive materials, the Laboratory has released low-level-radioactive liquid wastes to the Clinch River via Whiteoak Creek. The fate of these radioactive wastes and the mechanisms by which the contained radionuclides are dispersed in the river have been investigated through the Clinch River Study, a multiagency effort to evaluate the past, present, and future use of the river for disposal of such wastes (Pickering and others, 1965; Struxness and others, 1967). The participants in the study were: Oak Ridge National Laboratory, operated by Union Carbide Corp.; Tennessee Game and Fish Commission; Tennessee State Department of Public Health, Stream Pollution Control Board; Tennessee Valley Authority (TVA); U.S. Atomic Energy Commission (AEC); U.S. Geological Survey (USGS); U.S. Public Health Service (PHS).

When the study was begun in 1960, the following objectives were established by the Clinch River Study

Steering Committee, an advisory group composed of representatives of each of the participating agencies (Morton, 1963, p. 1): (1) To determine the fate of radioactive materials currently being discharged to the Clinch River, (2) to determine and understand the mechanisms of dispersion of radionuclides released to the river, (3) to evaluate the direct and indirect hazards of current disposal practices in the river, (4) to evaluate the overall usefulness of the river for radioactive waste disposal purposes, and (5) to provide appropriate conclusions regarding long-term monitoring procedures.

The release of low-level radioactive liquid waste to the basin of Whiteoak Creek, which drains the Oak Ridge National Laboratory area, was begun soon after establishment of the Laboratory in 1943. Radioactive liquids have entered Whiteoak Creek as a result of direct releases of processed waste water from the Laboratory, seepage from liquid waste pits, and drainage from solid waste disposal trenches (Browder, 1959).

Throughout most of the Laboratory's history, the waters of Whiteoak Creek have been impounded in Whiteoak Lake by Whiteoak Dam, which is 0.6 mile upstream from the mouth of the creek. The lake was created as a temporary storage facility for the radioactive waste carried in the creek water. Radioactive waste waters in Whiteoak Creek flow into the Clinch River at a point 3.3 miles downstream from the Laboratory area. The diluted wastes in the Clinch River flow into the Tennessee River 20.8 miles downstream from the entry of Whiteoak Creek.

The continuous release of radioactive wastes to the Clinch River during 20 years of Laboratory operations has provided a unique opportunity for studying the effects of such releases on the river, and the effects of the physical, chemical, hydrological, and biological characteristics of the river on the individual radionuclides. As one element of the study, the chemical compositions and variability of the streams that receive the radioactive wastes were characterized through an intensive program of water sampling. These water-quality characteristics are the subject of this report.

### ACKNOWLEDGMENTS

Analyses of the stable chemical compositions and the physical properties of samples of Clinch River water and Tennessee River water taken in the regular sampling program of the Clinch River Study were made at the chemical laboratory of the Tennessee Stream Pollution Control Board in Nashville, Tenn., under the direction of S. Leary Jones. Radiochemical analyses of aliquots of the same samples were made at facilities of the U.S. Public Health Service in Cincinnati, Ohio, by

personnel of the Division of Radiological Health. Stable chemical analyses of Whiteoak Creek water, analyses of Clinch River water for trace and minor elements, and nonregular radiochemical analyses were performed by personnel of the Analytical Chemistry Division, ORNL.

P. H. Carrigan, Jr., Project Chief of the Clinch River Study for the U.S. Geological Survey (USGS), has offered many valuable suggestions and much helpful advice pertaining to the study. Discussions of sorption mechanisms with T. Tamura (ORNL), V. C. Kennedy, (USGS), and E. A. Jenne (USGS) have been most helpful to the author, as have discussions of radioactivity in Whiteoak Creek with W. M. McMaster (USGS) and T. F. Lomenick (ORNL). The results of studies of the desorption of radionuclides from Whiteoak Creek bottom sediment, performed by W. P. Bonner (ORNL) and T. Tamura (ORNL), served as valuable references during the preparation of the report.

E. R. Eastwood (ORNL) was in charge of sampling and sample preparation for sampling stations on the Clinch River and Whiteoak Creek.

The basic digital computer program used in correlating the results of water analyses was written by A. M. Craig, Jr., ORNL Mathematics Division. Modifications of the basic program for special applications, and several additional programs used in the study, were prepared by P. H. Carrigan, Jr. (USGS) and the author. Calculations used for comparison of means and variances of stable chemical analyses at station pairs were performed by Mr. Carrigan.

The use of concise statistical summaries of the results of radiochemical analyses performed on water samples collected as part of the regular sampling program for the Clinch River Study, which were prepared under the direction of M. A. Churchill (TVA), expedited the study greatly.

Original drawings for figures 1 and 2 were prepared by the Graphic Arts Services Department, ORNL.

Work described in this report was part of a cooperative program with the Health Physics Division, Oak Ridge National Laboratory; the Oak Ridge Operations Office, U.S. Atomic Energy Commission; and the Division of Reactor Development and Technology, U.S. Atomic Energy Commission. Oak Ridge National Laboratory is operated for the U.S. Atomic Energy Commission by Union Carbide Corp.

## BASIS FOR THE SAMPLING PROGRAM

### CHEMICAL TRANSPORT IN STREAMS

A chemical element can be transported in a surface stream in two general ways: (1) In solution, either ionic

or molecular, and (or) (2) in suspension, through its association with solid particles ranging in size from colloidal dimensions to material several millimeters in diameter. The radioactive form of an element is essentially the same in its chemical combining properties as the nonradioactive form; thus, the chemical reactions in which the various radionuclides released by ORNL can take part in the receiving streams may be predicted on the basis of knowledge of the geochemical properties of those elements.

While still in transit in a stream, a chemical element may shift its association from solid to liquid phase, or from liquid to solid phase, as a result of a change in the chemical composition of the transporting water. Examples of such shifting are given in the following paragraphs.

1. Ions or molecules in solution can be sorbed [1] by solids in contact with the water through surface attraction due to van der Waals forces, or through specific or nonspecific ion exchange reactions. For example, strontium ions entering a stream in a waste solution can become attached to clay-mineral particles, which are present in bottom sediment and in suspension in the water, through the attraction of the negatively-charged crystal surfaces of clay-mineral particles for the positively-charged strontium ions (Baver, 1956, p. 24; Grim, 1953, p. 126–155). However, in molecular sorption, and in nonspecific ion exchange reactions such as the one just described, all dissolved molecules and ions must compete for exchange sites and surface positions with one another and with molecules or ions already associated with the solids (Sayre and others, 1963, p. 13). Divalent ions compete more effectively than do monovalent ions for exchange sites. In calcarous systems, such as exist in the three streams studied, ions of strontium-90 must compete with the more abundant calcium, magnesium, and stable strontium ions for exchange sites. Thus, dissolved radionuclides would not be expected to be removed very effectively from solution through uptake by stream sediment, unless uptake were by means of a specific sorption reaction.

   In specific sorption reactions, a particular ion or group of ions is sorbed preferentially, even when present in solution in relatively minor abundance. The uptake of cesium by mica and illite (Jacobs and Tamura, 1960) is an example of this sort of reaction. But even in specific sorption re-

actions involving only a single element, an individual radionuclide would be competing with the commonly more abundant stable forms of the same element in solution. Kennedy (1965) has described the control that sorption and desorption reactions of stream sediments exert on the chemical composition of a stream.

2. Precipitation of chemical compounds formed from ions in solution in a surface stream can take place as a result of changes in chemical composition, water temperature, dissolved-oxygen content, pH, or other stream-quality parameters. The precipitates formed in such a manner commonly contain small quantities of elements other than the primary elements of their compound as impurities. These minor constitutents may have been incorporated in the host precipitate by coprecipitation, by occlusion, or by substitution for another element in the crystal lattice of the precipitate. For example, strontium will substitute for calcium, to a limited extent, in the calcium carbonate minerals. Thus, if radiostrontium is present in water from which calcium carbonate is precipitating, some of the radiostrontium will be incorporated in the precipitate.

3. Dissolution of particles of a chemical precipitate and desorption of ions from sediment particles may occur when the chemical composition of the stream water is changed. Such compositional changes can occur as a result of dilution or mixing of one stream with another, or through release of chemical wastes to a stream.

From the above discussion, it should be apparent that the chemical and physical composition of a stream into which radioactive wastes are discharged can be an important factor in determining the fates, both temporary and ultimate, of the various introduced radionuclides. Stream processes that affect the fates of the introduced radionuclides are:

1. Transport of previously-formed radioactive solids.

2. Sorption of dissolved radionuclides by suspended solids present in water, or by solids in bottom sediment in contact with the water.

3. Competition of stable ions and molecules dissolved in the water with introduced radionuclides in nonspecific and specific sorption reactions.

4. Precipitation of radionuclide-bearing compounds as a result of oversaturation of the compounds in the water.

5. Dissolution or desorption of radionuclide-bearing solids as a result of a change in concentration of dissolved ions in the water.

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[1] Because the specific processes involved in the uptake of radioactive materials by stream sediment are for the most part not precisely known, the general term "sorption" has been used in this paper. For an explanation of the term, see Sayre, Guy, and Chamberlain (1963, p. 11) and McBain (1950, p. 38).

## EVIDENCE OF TRANSPORT OF RADIONUCLIDES IN SOLUTION

Evidence for removal of dissolved strontium-90 from river water through formation of calcium carbonate has been reported by Nelson (1962), who measured the radiostrontium-stable strontium ratio in clam shells in the Clinch River and the Tennessee River. He reported that the ratio decreases with distance downstream from the mouth of Whiteoak Creek in a manner consistent with predictions based on flow dilution. This relationship is apparently the result of proportional substitution of dissolved radiostrontium and stable strontium for some of the calcium ions in the calcium carbonate of the clam shell during its formation.

Further evidence of removal of strontium-90 from solution was provided by a deposit of calcite that formed as a coating on a metal object that had remained submerged in the Clinch River for 9 months at a point 1.5 miles downstream from the mouth of Whiteoak Creek. The calcite contained 123.9 picocuries per gram ruthenium-103 and -106 and 10.1 picocuries per gram strontium-90 (Parker, 1963). This radionuclide content is within the range of radioactivity commonly found in suspended sediment in Clinch River water downstream from the mouth of Whiteoak Creek.

Substantial amounts of strontium-90 have been desorbed from samples of Whiteoak Creek bottom sediment by neutral solutions containing ions that compete with the strontium ion for exchange positions (Morton, 1965. p. 53). These results indicate that strontium had been removed from solution by the sediment through nonspecific sorption reactions. Strontium held in this manner would be sensitive to changes in concentrations of competing ions in Whiteoak Creek water.

## EVIDENCE OF TRANSPORT OF RADIONUCLIDES IN ASSOCIATION WITH SUSPENDED SOLIDS

Jacobs (1960) and Tamura (1963) have described the preferential uptake, or sorption, of cesium ions by layered aluminosilicate minerals having a mica-type structure (Grim, 1953, p. 65) in which the spacing in the direction of the crystallographic c-axis is 10 angstroms. Desorption studies have indicated that once cesium ions have been sorbed in this manner by stream sediment, they are not readily removed by leaching (Morton, 1965, p. 53–55). Most of the cesium-137 entering the Clinch River by way of Whiteoak Creek is associated with suspended solids, presumably aluminosilicate minerals, in the water, and this association persists throughout the lower Clinch River (Churchill and others, 1965, p. 37). The reservoir of cesium-137 that exists in the bottom sediment of Whiteoak Lake (Lomenick and Gardiner, 1965) is evidence that much of the cesium entering Whiteoak Creek from the Oak Ridge National Laboratory as a dissolved ion soon becomes incorporated in suspended or bottom sediment in the creek.

Sediment suspended in a stream will be carried to a point of deposition that is governed by the size of the suspended particles and the velocity and turbulence of the water. At times of high streamflow, resuspension and downstream movement of the cesium-bearing sediment can occur. A pattern of movement of this sort is consistent with the observed occurrence of cesium-137 in the Clinch-Tennessee river system (Cottrell, 1959; Pickering and others, 1966).

Whiteoak Creek bottom sediment contains cobalt-60 that can be removed from the sediment only by highly acidic solutions (Morton, 1965, p. 53). This characteristic suggests that the radionuclide was incorporated in the bottom sediment, and therefore probably in suspended sediment as well, by either a sorption reaction that is specific for cobalt, or by another solids-forming process such as the precipitation of a relatively insoluble chemical compound containing cobalt. Jenne and Wahlberg (1965, 1968) have reported that much of the cobalt-60 in Whiteoak Creek bottom sediment is associated with manganese and iron oxides, both relatively insoluble groups of minerals. Sorathesn and others (1960) have suggested that cobalt-60 may be sorbed by organic matter. Such solids probably have provided a vehicle for the transportation of cobalt-60 in the Clinch-Tennessee river system. The close relationship between concentrations of cobalt-60 and cesium-137 that has been observed in Clinch River bottom sediment (Pickering, 1969) indicated that some cobalt-60 enters the Clinch River in the form of solid particles, and the limited removal of the cobalt by solutions containing competing ions suggests that simple ion exchange is not the primary means by which cobalt is incorporated in the sediment.

Most of the ruthenium-106 released to Whiteoak Creek enters as seepage from high-nitrate waste solutions contained in liquid waste disposal pits (Lomenick, 1963; Morton, 1963, p. 19). Studies of simulated waste solutions (Lomenick, 1963), and leaching experiments performed on bottom sediment from Whiteoak Creek (Morton, 1965, p. 60–62), indicate that some of the ruthenium may be present in the form of nitrosyl ruthenium hydroxide—$RuNO(OH)_3(H_2O)_2$. The chemical behavior of the hydroxide is not well known, but it is probably not easily dissolved in dilute, near-neutral waters (Story and Gloyna, 1963) like those of the lower part of Whiteoak Creek and the Clinch River. Its transport in the river system as a very fine suspended precipitate (less than 0.7 micron) is therefore likely.

## LOCATION AND OPERATION OF WATER-SAMPLING STATIONS

Radioactive wastes from ORNL are released to Whiteoak Creek, which enters the Clinch River 20.8 miles upstream from where the Clinch River enters the Tennessee River. In order to characterize the composition and variability of each of the three streams, water samples were collected for 1- or 2-year periods at seven sampling stations, and analyzed for their content of stable chemical constituents, radiochemical constituents, and suspended sediment. Sampling was begun in December 1960 and concluded in November 1963.

The locations of the sampling stations are listed in table 1 and shown in figures 1 and 2. One water sampling station was at Whiteoak Dam, 0.6 mile upstream from the mouth of Whiteoak Creek, three stations were on the Clinch River, and three stations were on the Tennessee River. The most upstream stations on both the Clinch River and the Tennessee River were at points not affected by releases of radioactive wastes from ORNL, and served as background stations for the water sampling program. The entire reach of the Clinch River below the mouth of Whiteoak Creek is an arm of Watts Bar Lake, which is formed by Watts Bar Dam on the Tennessee River (fig. 2).
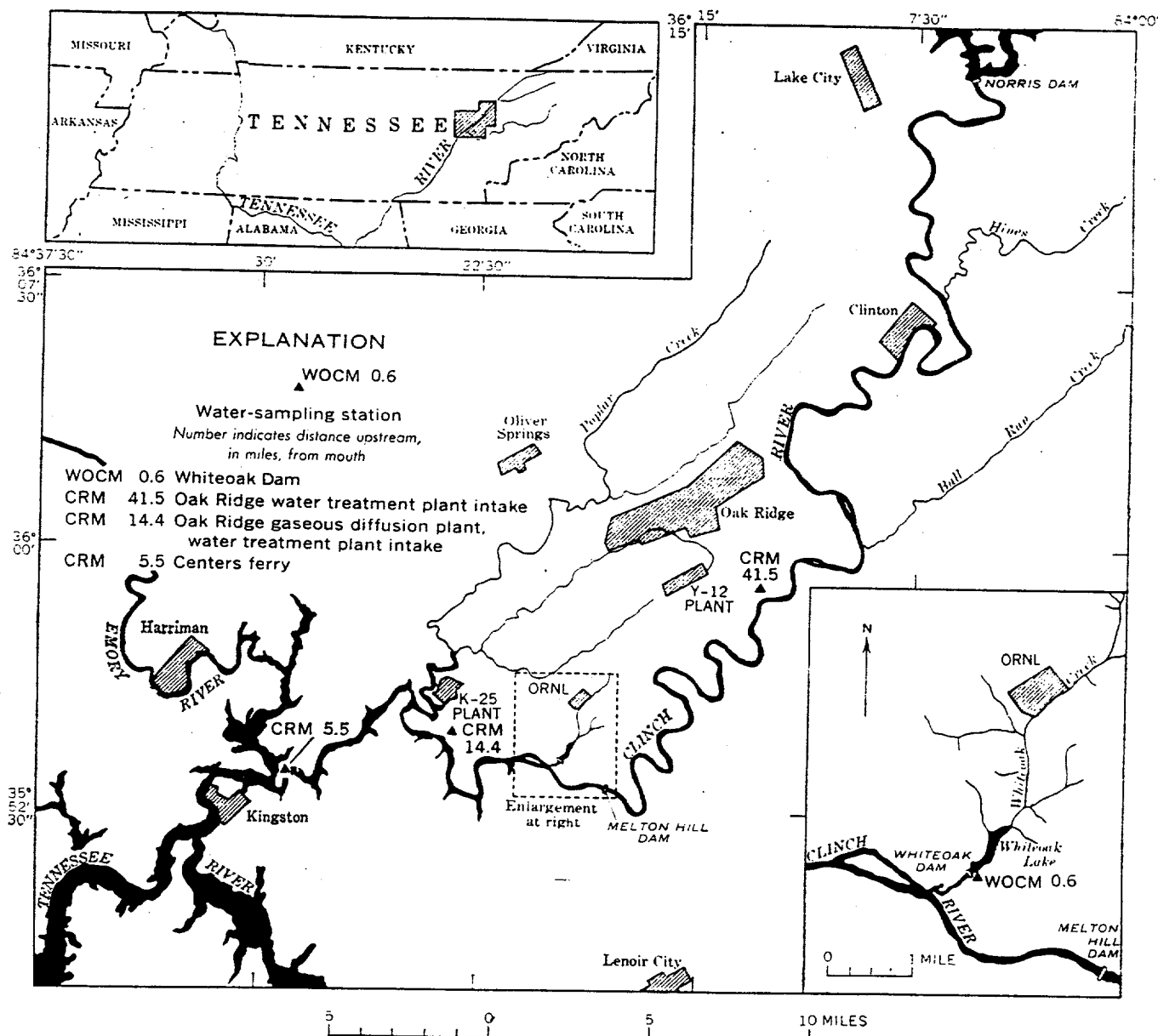


FIGURE 1.—Locations of water-sampling stations on the Clinch River and on Whiteoak Creek.

TABLE 1.—*Locations of water-sampling stations*

| Location | Stream | Stream mile [1] |
|---|---|---|
| Overflow at Whiteoak Dam. | Whiteoak Creek | WOCM | 0. 6 |
| Oak Ridge water treatment plant intake. | Clinch River | CRM | 41. 5 |
| Oak Ridge gaseous diffusion plant water treatment plant intake. | _____do_____ | CRM | 14. 4 |
| Centers Ferry | _____do_____ | CRM | 5. 5 |
| Loudon, Tenn | Tennessee River | TRM | 591. 8 |
| Tailrace at Watts Bar Dam. | _____do_____ | TRM | 529. 9 |
| Tailrace at Chickamauga Dam. | _____do_____ | TRM | 471. 0 |

[1] The abbreviation "CRM" (Clinch River mile), followed by a figure, is used in this report to designate distance upstream, in miles, from the mouth of the Clinch River. Similarly, "TRM" (Tennessee River mile) and "WOCM" (Whiteoak Creek mile), followed by figures, also designate distance from the mouths of the streams. This terminology is consistent with prior usage in the Clinch River Study (Morton, 1961, 1962b).

A history of sample collection, preparation, and analysis for each sampling station is shown graphically in figure 3. At the beginning of the project, water samples from the stations at TRM 529.9, TRM 471.0, CRM 41.5, CRM 5.5, and WOCM 0.6 were collected

one or more times daily and composited into weekly samples (7-day composites) on the basis of discharge in the stream at the time of collection (Churchill and others, 1965). After the first 5 months of sampling had been completed at the first three stations, preparation of composite samples for stable chemical analysis was reduced to a monthly basis (30-day composites). At the station at CRM 5.5, 7-day composite samples were prepared throughout the entire 2-year sampling period. At the background station on the Tennessee River (TRM 591.8), equal increments of daily samples were composited into non-discharge-weighted monthly samples (30-day composites) during the entire sampling period and analyzed for both stable chemical and radiochemical constituents. Radiochemical analyses were made of discharge-weighted 7-day composite samples from all sampling stations except the station at TRM 591.8.

The water-sampling station at CRM 14.4 was operated as part of the Clinch River Study only during the second year of the sampling period, and only radiochemical analyses of discharge-weighted 7-day composite samples were made. However, stable chemical
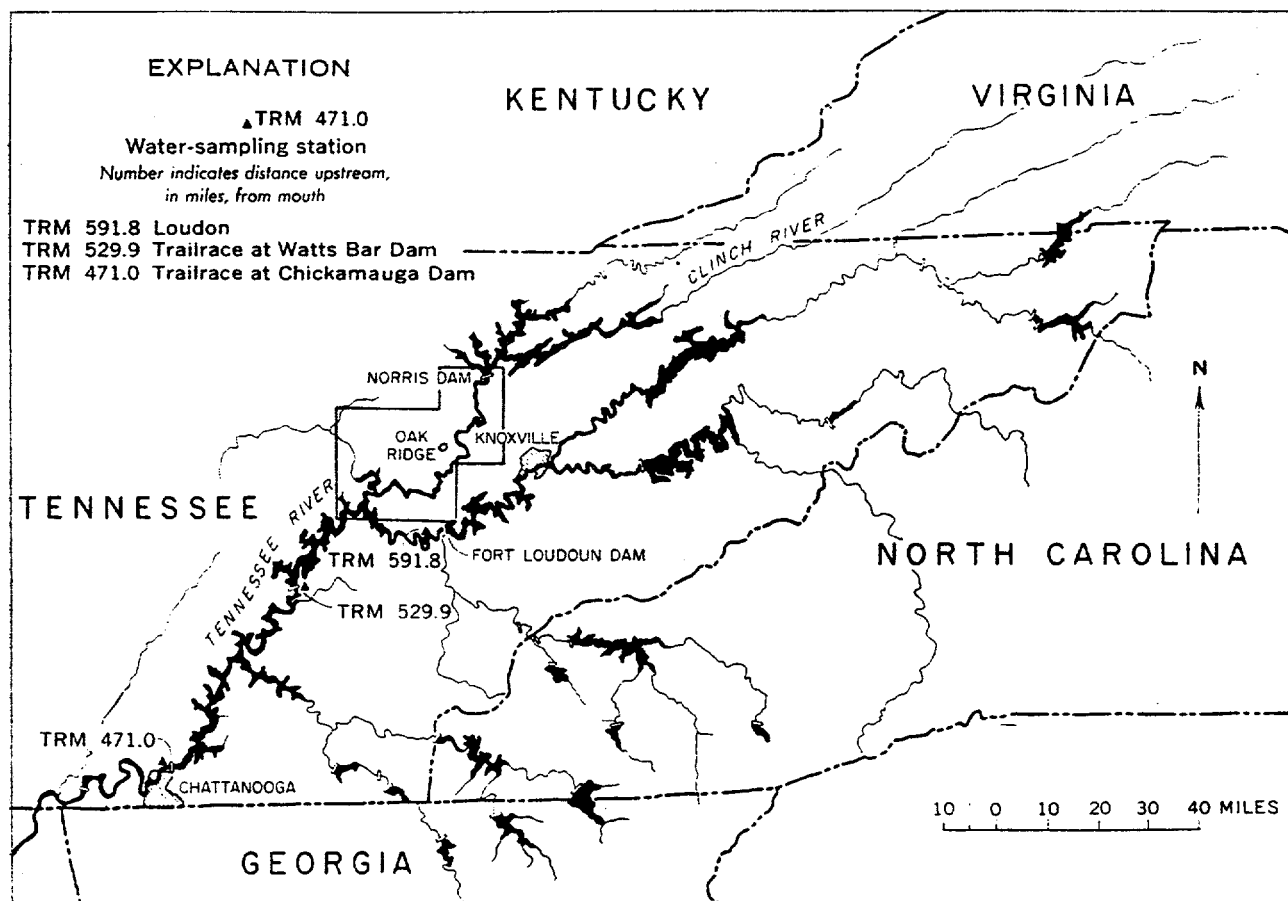


FIGURE 2.—Locations of water-sampling stations on the Tennessee River. Outline shows area of figure 1.

analyses of non-discharge-weighted 7-day composite samples from that station had been made during the preceding year at facilities of the Analytical Chemistry Division, ORNL, and have been included in the data used in this report. No stable chemical analyses were made of samples from the sampling station at White-oak Dam (WOCM 0.6) as part of the regular water-sampling program of the Clinch River Study, but analyses of samples collected during a later, noncoincident period, November 1962 through November 1963, made at facilities of the Analytical Chemistry Division, ORNL, are included in this report.

The intake at each water-sampling station was located at a point in the stream channel where mixing was believed to be complete and a homogeneous sample of the stream could be obtained. Samples were not preserved in any way, and although the dilute nature of the water in all three streams may have served to minimize compositional changes that occurred between the time of collection and the time of analysis, some changes probably took place nonetheless. These changes, which were assumed to be minor, were made less significant by the preparation of composite samples.

Stable chemical analyses were performed on raw water samples at all stations except the stations at WOCM 0.6 and CRM 14.4, for which analyses were run on filtered samples. Analyses for stable strontium at all sampling stations were performed on filtered samples.



EXPLANATION

CRM 41.5. water-sampling station
S. stable chemical analyses
R. radiochemical analyses

7-day composite samples

Not discharge weighted

Discharge weighted

30-day composite samples

Not discharge weighted

Discharge weighted

FIGURE 3.—History of sampling and analysis of water for Clinch River Study.
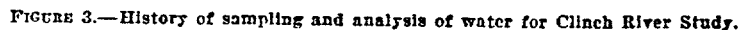
Determinations of the physical properties and the content of major and minor elements in the water samples from the stations at CRM 41.5, CRM 5.5, TRM 591.8, TRM 529.9, and TRM 471.0 were made at the chemical laboratory of the Tennessee Stream Pollution Control Board, Nashville, Tenn. Determinations of the content of trace elements in the samples were made at facilities of the Analytical Chemistry Division, ORNL. Radiochemical analyses of the samples were performed by personnel of the Division of Radiological Health, U.S. Public Health Service (USPHS), Cincinnati, Ohio. Most of the analytical methods used have been described in publications of the respective agencies (see Tennessee Stream Pollution Control Board, 1960; Rains and others, 1962; Feldman and Rains, 1964; Porter and others, 1965; Hallbach, 1959).

## STABLE CHEMICAL COMPOSITION OF WATER

### CLINCH RIVER WATER

Partial results of stable chemical analyses of composite samples of Clinch River water prepared during the 2-year sampling period as part of the Clinch River Study have been reported by Morton (1962a, b), the Tennessee Stream Pollution Control Board (1960, 1961, 1962), and the Tennessee Valley Authority (1963). A statistical summary of the results of all analyses is given in table 2. Maximums, minimums, and standard deviations listed in table 2 are for composite samples and thus do not represent the full range of compositional variability of the stream.

In this report, the units which indicate concentrations of dissolved solids and individual ions determined by chemical analysis are reported both in the English and metric systems. This change from reporting in "English units" has been made as a part of a gradual change to the metric system that is in general use by the scientific community. The change is intended to promote greater uniformity in reporting of data. Chemical data on concentrations are reported in both milligrams per liter (mg/l) and in parts per million (ppm), the units used in earlier reports in this series. For concentrations less than 7,000 mg/l, the numbers reported are about the same as for concentrations in parts per million.

TABLE 2.—Summary of stable chemical analyses of composite samples of Clinch River water [1]

| | Clinch River mile 41.5 — 24 months [2] | | | | Clinch River mile 14.4 — 58 weeks [3] | | | | | Clinch River mile 5.5 — 104 weeks [4] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | Standard deviation monthly [4] | Minimum | Maximum | Mean | Standard deviation weekly [6] | Standard deviation monthly [5] | Minimum | Maximum | Mean | Standard deviation weekly [6] | Standard deviation monthly [4] | Minimum | Maximum |
| Turbidity, ppm (mg/l) | 28 | 19 | 6 | 68 | [7] | — | — | — | — | 17 | 16 | 10 | 1 | 86 |
| Apparent color, ppm (mg/l) | 197 | 124 | 42 | 542 | — | — | — | — | — | 114 | 97 | 50 | 3 | 480 |
| Centrifuged color, ppm (mg/l) | 20 | 15 | 0 | 62 | — | — | — | — | — | 20 | 20 | 14 | 0 | 102 |
| pH | [8] | [8] | 7.1 | 8.2 | [8] | [8] | .14 | 7.0 | 8.1 | [8] | [8] | [8] | 7.2 | 8.5 |
| HCO₃, ppm (mg/l) | 117 | 7.41 | 105 | 130 | 119 | 11.3 | 6.08 | 87 | 141 | 112 | 13.4 | 7.86 | 57 | 135 |
| Acidity, as CaCO₃, ppm (mg/l) | 3 | 3 | 0 | 10 | — | — | — | — | — | 4 | 3 | 2 | 0 | 14 |
| Hardness, as CaCO₃, ppm (mg/l) | 107 | 17.4 | 78 | 148 | — | — | — | — | — | 106 | 23.8 | 19.7 | 69 | 169 |
| Ca, ppm (mg/l) | 27 | 4.3 | 18 | 36 | 21 | 2.4 | 1.8 | 17 | 27 | 27 | 5.2 | 3.8 | 17 | 43 |
| Mg, ppm (mg/l) | 9.4 | 2.8 | 5.1 | 18.0 | 7.7 | 1.0 | .71 | 4.5 | 10.0 | 9.4 | 3.7 | 2.8 | 4.1 | 22.6 |
| Cl, ppm (mg/l) | 5 | 2 | 1 | 11 | 1.6 | .53 | .30 | 1.0 | 4.5 | 3 | 1 | .9 | 1 | 8 |
| SO₄, ppm (mg/l) | 12 | 5 | 2 | 23 | 10 | 4 | 1.5 | 1.0 | 27 | 12 | 5 | 3 | 0 | 29 |
| NO₃, ppm (mg/l) | 1.0 | .59 | .2 | 2.4 | 2.7 | 4.0 | 3.0 | .3 | 19 | 1.5 | 1.7 | 2.2 | .0 | 12.7 |
| Fe, ppm (mg/l) | 3.4 | 2.3 | .3 | 9.2 | .06 | .08 | .06 | .01 | .37 | 1.7 | 1.3 | .80 | .1 | 7.1 |
| PO₄, ppm (mg/l) | .2 | .09 | .1 | .4 | .22 | .17 | .10 | .05 | .75 | .1 | .1 | .07 | .0 | .6 |
| K, ppm (mg/l) | 1.7 | .49 | .8 | 3.1 | 1.3 | .20 | .13 | 1.1 | 2.3 | 1.6 | .55 | .42 | .6 | 3.5 |
| Na, ppm (mg/l) | 2.3 | 1.1 | 1.0 | 5.2 | 2.4 | .50 | .39 | 1.8 | 4.7 | 2.4 | 1.3 | .90 | .0 | 9.5 |
| Si, ppm (mg/l) | 2.9 | .69 | 1.5 | 4.0 | 1.5 | .72 | .68 | .1 | 2.4 | 2.7 | .63 | .42 | .9 | 4.4 |
| Specific conductance at 25° C, μmhos | 195 | 36.5 | 119 | 263 | 216 | 14.4 | 9.98 | 190 | 282 | 196 | 42.8 | 36.5 | 105 | 312 |
| Suspended solids, ppm (mg/l) | 185 | 124 | 18 | 557 | 25.3 | 20.3 | 14.5 | 1.0 | 104 | 55 | 46 | 32 | 2 | 275 |
| Dissolved solids, ppm (mg/l) | 125 | 27 | 67 | 201 | 129 | 20.7 | 8.43 | 90 | 218 | 133 | 64 | 37 | 25 | 549 |
| Total solids, ppm (mg/l) | 310 | 121 | 140 | 677 | 154 | 23.6 | 14.9 | 127 | 231 | 188 | 77 | 49 | 112 | 601 |
| Kjeldahl N, as N, ppm (mg/l) | .7 | .2 | .3 | 1.3 | — | — | — | — | — | .5 | .3 | .2 | .2 | 1.7 |
| Mn, ppm (mg/l) | .4 | .3 | .0 | 1.1 | — | — | — | — | — | [10].1 | [10].1 | [11].03 | [10].00 | [10].6 |
| Cr, ppm (mg/l) | [9].02 | [9].05 | [9].00 | [9].19 | — | — | — | — | — | [10].1 | [10].03 | [11].03 | [10].00 | [10].18 |
| Sr, ppm [1] (mg/l) | [12].073 | [12].0068 | [12].058 | | .07 | .009 | .0067 | .040 | .080 | .069 | .0076 | .0055 | .043 | .080 |
| Discharge, cfs [13] | 5,000 | 2,780 | 2,610 | 14,280 | 4,620 | 2,525 | 1,680 | 545 | 15,990 | 5,580 | 3,853 | 3,060 | 359 | 19,000 |

[1] Chemical analyses of filtered samples for Sr by ORNL. Chemical analyses of centrifuged samples from CRM 14.4 for all other constituents by ORNL. All other chemical analyses of raw samples by Tennessee Stream Pollution Control Board.
[2] Sampling period, December 1960 through November 1962. Samples were discharge weighted.
[3] Sampling period, Nov. 28–Dec. 4, 1960, through Jan. 3–8, 1962. Maximum, minimum, and mean are for 7-day composite samples. Samples were not discharge weighted.
[4] Sampling period, Nov. 27–Dec. 3, 1960, through Nov. 25–Dec. 1, 1962. Maximum, minimum, and mean are for 7-day composite samples. Samples were discharge weighted.
[5] Standard deviation of 30-day composite samples from mean for sampling period.
[6] Standard deviation of 7-day composite samples from mean for sampling period.
[7] Dash indicates that constituent was not determined.
[8] Not calculated.
[9] Sampled for 19-month period only, May 1961 through November 1962.
[10] Sampled for 85-week period only, Apr. 16–22, 1961, through Nov. 25–Dec. 1, 1962.
[11] For 19-month period only, May 1961 through November 1962.
[12] Sampled for 42-week period, Mar. 19–25, 1961, through Dec. 31, 1961–Jan. 6, 1962. Maximum, minimum, mean, and standard deviation are for 7-day composite samples.
[13] Not discharge weighted. Discharge data are time weighted.

Calcium is the predominant dissolved cation in Clinch River water, and bicarbonate is the predominant anion. The chemical composition of the water presumably is the result of the abundance of limestone and dolomite in bedrock underlying the drainage basin of the Clinch River.

Analytical results for all three sampling stations are very similar. Different water velocities at the most upstream and the most downstream sampling stations probably account for differences in mean turbidity, suspended solids, and iron content at the two stations. Iron and manganese in the water appear to be associated with suspended solids which settle out of the water as velocity decreases with distance downstream. Differences in nitrate content between the two stations probably reflect local differences in use of fertilizer on farmland drained by the river. Differences between some of the mean values for the sampling station at CRM 14.4 and the other two stations are probably the result of different total sampling periods and different methods of sample processing at the two laboratories involved. (See footnotes accompanying table 2.)

Periodic analyses of composite water samples from CRM 14.4 for trace and minor elements were made by the spectrographic laboratory at ORNL during an 11-month period from February 6, 1961, through January 8, 1962. The results of these analyses are summarized in table 3. Water samples composited on a weekly basis (not discharge weighted) were analyzed for cesium, cobalt, ruthenium, and hexavalent chromium, and ap-

proximately every third composite sample was analyzed for copper, rubidium, ammonium, zinc, barium, aluminum, manganese, titanium, zirconium, nickel, fluoride, bromide, iodide, lithium, and beryllium.

Discharge-weighted mean monthly concentrations of stable chemical constituents were computed for the three stations on the Clinch River, plotted, and examined for seasonal variations. Turbidity, apparent color, centrifuged color, suspended solids, and iron, all largely controlled by seasonal variations in rainfall and surface runoff, varied in the same general manner as discharge in the river, being highest in late winter and early spring. Hardness, calcium, magnesium, sodium, and chloride showed maximum concentrations in the autumn, when ground-water contribution was the maximum percentage of total flow, and minimum concentrations in the spring, when much of the flow came from surface runoff. Organic nitrogen (Kjeldahl method) reached a maximum in the early summer. Sporadic high concentrations of nitrate that occurred in spring are assumed to reflect the use of nitrate fertilizers on farmland draining into the river. Potassium showed a maximum in the spring, and silica showed a maximum in the summer and a minimum in the winter. Examples of seasonal variations in selected constituents at CRM 41.5 are shown graphically in figure 4.

## WHITEOAK CREEK WATER

A statistical summary of the chemical composition of Whiteoak Creek water is shown in table 4. The data are based on 27 7-day composite samples of water passing over Whiteoak Dam (WOCM 0.6). The samples were collected over a period of 1 year by means of a sampling device which took samples that were proportional to the discharge over the dam (Abee and Hart, 1961). The composite samples for the determination of major and minor element concentrations were collected every other week during the 1-year period. Samples for trace-element analysis (strontium, cesium, and rubidium) were collected during the alternate weeks. The sampling period for Whiteoak Creek water was not coincident with that for Clinch River water and Tennessee River water, as noted in a preceding section of this report.

Whiteoak Creek water is a calcium bicarbonate water that is similar in composition to Clinch River water but is more highly mineralized. It has a higher content of sulfate, nitrate, phosphorus, and sodium than does Clinch River water. It appears also to have a somewhat higher average content of bicarbonate and calcium, and a somewhat lower content of magnesium, but minor differences in composition cannot be adequately defined due to lack of concurrence of the sampling periods.

TABLE 3.—*Summary of analyses of composite samples of Clinch River water for trace and minor elements* [1]

|  | Mean [2] | Minimum | Maximum | Number of analyses |
|---|---|---|---|---|
| Cs | <0.01 | | | 43 |
| Co | [3] <.02 | | | 43 |
| Ru | <.1 | | | 43 |
| Cu | | <0.01 | 0.10 | 14 |
| Rb | <.005 | | | 15 |
| NH$_4$ | | <.02 | .11 | 14 |
| Zn | .11 | .05 | .32 | 13 |
| Ba | [4] <.3 | | | 19 |
| Al | | <.01 | .34 | 15 |
| Mn | <.01 | | | 17 |
| Ti | | <.01 | .08 | 16 |
| Zr | .03 | .01 | .06 | 19 |
| Ni | | <.01 | .03 | 14 |
| F | | <.05 | .38 | 14 |
| Br | <1 | | | 6 |
| I | <2 | | | 5 |
| Li | .005 | .004 | .007 | 3 |
| Be | | <.001 | .005 | 3 |
| Cr, hexavalent [5] | <.01 | | | 20 |

[1] Chemical analyses of 7-day composite samples collected at CRM 14.4. Sampling period Feb. 6, 1961, through Jan. 8, 1962. Chemical analysis by Spectrographic Laboratory, ORNL. Concentrations in parts per million (milligrams per liter).
[2] Where mean value is given as less than a stated number, all measured concentrations were less than the stated minimum detectable concentration.
[3] <0.01 beginning Aug. 14, 1961. All analyses less than minimum detectable concentration.
[4] <0.05 beginning July 10, 1961. All analyses less than minimum detectable concentration.
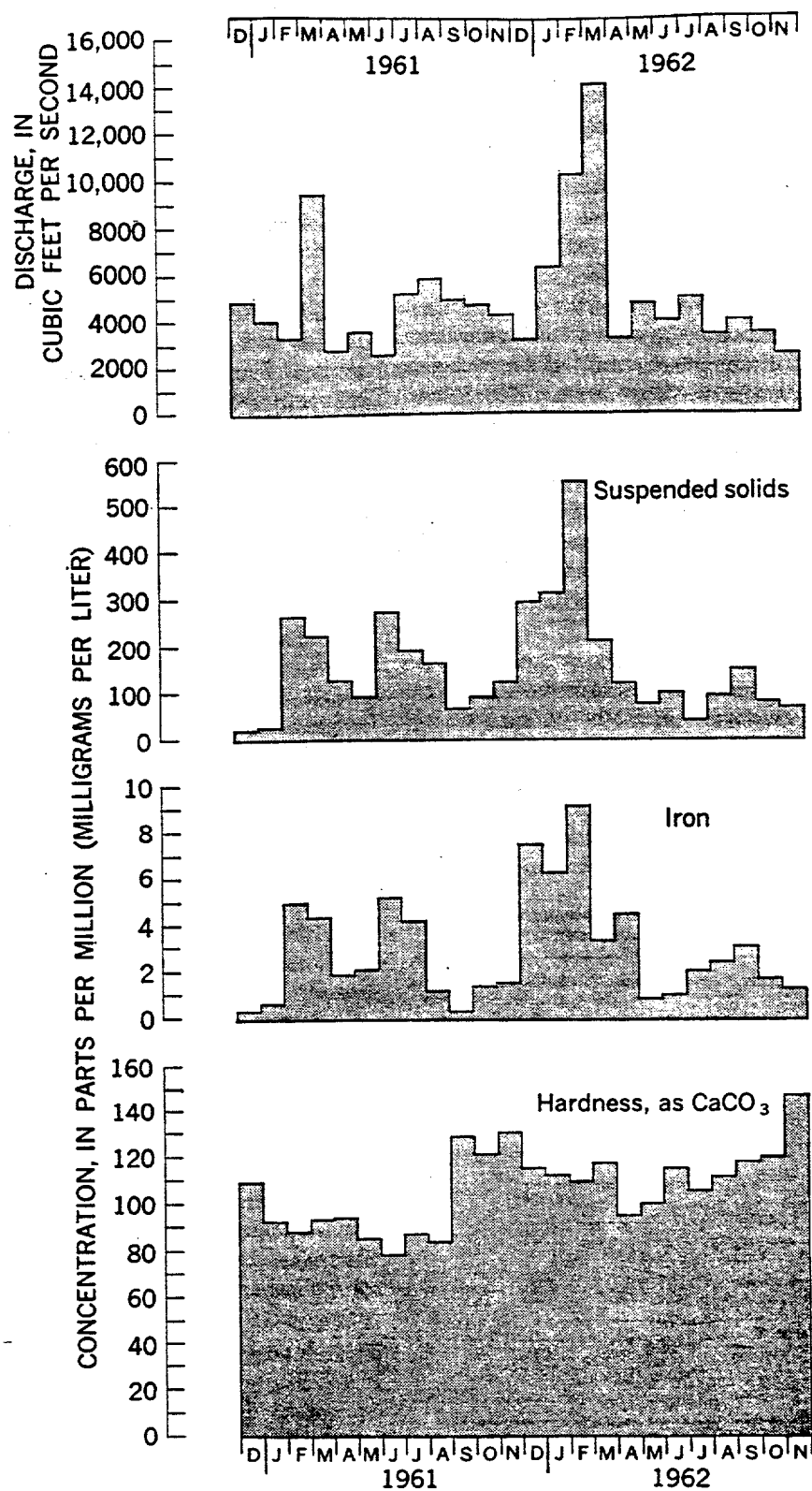[5] Sampling period Aug. 7, 1961, through Jan. 8, 1962.

FIGURE 4.—Seasonal variations of selected constituents in Clinch River water at CRM 41.5.

TABLE 4.—*Summary of stable chemical analyses of composite samples of Whiteoak Creek water* [1]

| | Mean | Standard deviation | Minimum | Maximum |
|---|---|---|---|---|
| pH | (²) | (²) | 7.2 | 8.0 |
| HCO₃, ppm (mg/l) | 125 | 24.2 | 79 | 168 |
| Ca, ppm (mg/l) | 32 | 4.6 | 22 | 40 |
| Mg, ppm (mg/l) | 6.0 | 1.7 | 3.1 | 9.1 |
| Cl, ppm (mg/l) | 5.1 | 2.0 | 2.4 | 9.7 |
| SO₄, ppm (mg/l) | 23 | 6.4 | 17 | 39 |
| NO₃, ppm (mg/l) | 8.2 | 5.8 | 1.8 | 25 |
| Fe, ppm (mg/l) | .08 | .1 | .01 | .44 |
| PO₄, ppm (mg/l) | .60 | 1.2 | .16 | .79 |
| K, ppm (mg/l) | 1.6 | .30 | .91 | 2.1 |
| Na, ppm (mg/l) | 14 | 7.8 | 4.1 | 32 |
| Si, ppm (mg/l) | 1.7 | .87 | .04 | 2.6 |
| Specific conductance at 25°C, μmhos | 283 | 60.3 | 160 | 410 |
| F, ppm (mg/l) | .50 | .31 | .26 | 1.2 |
| Cr, hexavalent, ppm (mg/l) | .01 | .007 | .005 | .04 |
| Sr, ppm (mg/l) | .065 | .012 | .050 | .100 |
| Cs, ppm (mg/l) | .00016 | .00041 | <.00001 | .0020 |
| Rb, ppm (mg/l) | .0013 | .0025 | .00013 | .0096 |
| Al, ppm (mg/l) | .10 | .076 | .006 | .30 |
| Li, ppm (mg/l) | .0057 | .0081 | .001 | .042 |
| Discharge, cfs | 14 | 4.3 | 5.1 | 87 |

[1] Sampling period Nov. 18-25, 1962, through Nov. 24-30, 1963. Chemical analyses of 7-day composite samples prepared every other week (27 samples for each constituent) from samples collected at Whiteoak Dam (WOCM 0.6). Samples for analysis of Sr, Cs, and Rb were not taken in same weeks as samples for analysis of the other constituents. Data discharge weighted except for discharge, which is time weighted. Chemical analysis by ORNL on filtered samples.
² Not calculated.

Some of the compositional differences no doubt are due to the release to Whiteoak Creek of liquid wastes from chemical processing operations at ORNL. No well-defined seasonal variations in constituent concentrations in Whiteoak Creek water were observed.

The entry of Whiteoak Creek into the Clinch River would be expected to have little measurable effect on the composition of Clinch River water because of the high dilution (mean, 670:1) of the creek water by the river water. However, the resulting change in the chemical environment of solids suspended in Whiteoak Creek water could induce such reactions in the solids as the release of sorbed ions or the dissolution of precipitates (for example, calcium carbonate).

### TENNESSEE RIVER WATER

Partial results of stable chemical analyses of composite samples of Tennessee River water prepared during the 2-year sampling period have been reported by Morton (1962a, b), the Tennessee Stream Pollution Control Board (1960, 1961, 1962), and the Tennessee Valley Authority (1963). A statistical summary of the results of all analyses is given in table 5. As noted before, maximums, minimums, and standard deviations are for composite samples and thus do not represent the full range of variability of the stream. A comparison of tables 2 and 5 indicates that although Tennessee

River water is a calcium bicarbonate type similar to Clinch River water, it contains somewhat less calcium, magnesium, bicarbonate, and suspended solids, and somewhat more sodium and chloride, than does Clinch River water.

The decrease in turbidity and iron content between the background station (TRM 591.8) and the two downstream stations at Watts Bar Dam (TRM 529.9) and Chickamauga Dam (TRM 471.0) was probably due to the settling out of suspended solids caused by decreased water velocities in the reservoirs upstream from the two dams. The higher content of sodium and chloride in Tennessee River water, as compared to Clinch River water, is probably due to chemical wastes from industries upstream from TRM 591.8. Dilution of Clinch River water by Tennessee River water is approximately sixfold.

An examination of plots of discharge-weighted mean monthly concentrations of stable chemical constituents at the sampling stations on the Tennessee River showed that turbidity, apparent color, centrifuged color, suspended solids, and iron varied in the same manner as discharge, which is largely controlled by seasonal variations in rainfall and runoff, as in the Clinch River. Hardness, calcium, magnesium, sodium, chloride, sulfate, and dissolved solids showed maximum concentrations in the autumn and minimum concentrations in the spring, probably due to the relatively great contribution of groundwater to streamflow, and decreased dilution of wastes, during the dry autumn months. Sporadic high concentrations of nitrate in Tennessee River water during the summer probably resulted from agricultural application of fertilizer. Potassium showed maxima in both spring and autumn, and silica showed a maximum in the autumn and a minimum in the winter. It may be that the latter two constituents are present both in association with suspended solids and in solution.

### CONSTITUENT COMPARISONS AND INTERSTATION COMPARISONS

Concurrent variations in concentration were statistically compared for each constituent pair at each sampling station. Turbidity, apparent color, and centrifuged color varied in a manner similar to that of suspended solids in the Clinch and Tennessee Rivers, as expected. Iron and manganese, and at some stations silica and potassium, varied in the same manner. This variation suggests that those constituents are present in the water primarily in association with solid particles. This association was confirmed for iron and manganese by the considerably lower contents of the two elements in samples from CRM 14.4 than in samples from other stations on the Clinch River. Most of the suspended solids were removed from the samples collected at CRM 14.4

TABLE 5.—*Summary of stable chemical analyses of composite samples of Tennessee River water* [1]

| | TRM 591.8 | | | | TRM 529.9 | | | | TRM 471.0 | | | |
| | 28 months [2] | | | | 24 months [3] | | | | 24 months [3] | | | |
| | Mean | Standard deviation monthly [4] | Minimum | Maximum | Mean | Standard deviation monthly [4] | Minimum | Maximum | Mean | Standard deviation monthly [4] | Minimum | Maximum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Turbidity, ppm (mg/l) | 14 | 11 | 3 | 52 | 6 | 7 | 1 | 29 | 7 | 9 | 1 | 35 |
| Apparent color, ppm (mg/l) | 88 | 58 | 34 | 272 | 53 | 49 | 5 | 226 | 59 | 52 | 8 | 223 |
| Centrifuged color, ppm (mg/l) | 23 | 21 | 5 | 95 | 24 | 23 | 0 | 108 | 31 | 27 | 5 | 118 |
| pH | (5) | (5) | 7.1 | 8.2 | (5) | (5) | 7.2 | 7.9 | (5) | (5) | 6.6 | 8.2 |
| HCO3, ppm (mg/l) | 66 | 10 | 50 | 95 | 70 | 7.6 | 52 | 82 | 63 | 8.8 | 44 | 87 |
| Acidity, as CaCO3, ppm (mg/l) | 3 | 2 | 0 | 8 | 3 | 2 | 1 | 10 | 3 | 2 | 0 | 5 |
| Hardness, as CaCO3, ppm (mg/l) | 75 | 18 | 49 | 138 | 75 | 18 | 47 | 127 | 70 | 17 | 44 | 115 |
| Ca, ppm (mgl) | 21 | 4.7 | 13 | 34 | 20 | 4.5 | 14 | 30 | 19 | 4.3 | 12 | 29 |
| Mg, ppm (mg/l) | 5.5 | 2.8 | 2.7 | 15.8 | 5.8 | 2.8 | 1.7 | 13.1 | 5.5 | 2.1 | 2.4 | 10.2 |
| Cl, ppm (mg/l) | 20 | 9 | 5 | 39 | 15 | 7 | 5 | 32 | 13 | 5 | 6 | 24 |
| SO4, ppm (mg/l) | 11 | 4 | 1 | 19 | 12 | 3 | 8 | 21 | 12 | 5 | 8 | 32 |
| NO3, ppm (mg/l) | 1.8 | 1.9 | .4 | 10.4 | 1.6 | 2.7 | .4 | 14.4 | 1.5 | 3.1 | .0 | 16.3 |
| Fe, ppm (mg/l) | 1.0 | .75 | .3 | 3.4 | .5 | .5 | .0 | 1.9 | .6 | .6 | .1 | 2.1 |
| PO4, ppm (mg/l) | .2 | .2 | .0 | 1.1 | .2 | .1 | .0 | .4 | .1 | .08 | .0 | .4 |
| K, ppm (mg/l) | 1.3 | .41 | .5 | 2.5 | 1.8 | .84 | .8 | 4.8 | 1.3 | .33 | .7 | 2.0 |
| Na, ppm (mg/l) | 9.5 | 3.7 | 3.9 | 16.0 | 6.8 | 2.7 | 2.9 | 12.0 | 5.8 | 2.4 | 1.7 | 11.3 |
| Si, ppm (mg/l) | 3.5 | .54 | 2.4 | 4.7 | 3.1 | .48 | 1.8 | 3.8 | 3.4 | .38 | 2.6 | 4.1 |
| Specific conductance at 25°C, μmhos | 170 | 31.9 | 122 | 247 | 177 | 33.6 | 115 | 247 | 162 | 26.9 | 128 | 221 |
| Suspended solids, ppm (mg/l) | 22 | 13 | 0 | 65 | 15 | 13 | 1 | 43 | 9 | 12 | 1 | 44 |
| Dissolved solids, ppm (mg/l) | 121 | 27 | 75 | 177 | 112 | 19 | 79 | 149 | 101 | 19 | 71 | 131 |
| Total solids, ppm (mg/l) | 142 | 25 | 105 | 189 | 126 | 18 | 83 | 156 | 111 | 17 | 75 | 138 |
| Kjeldahl N, as N, ppm (mg/l) | (6) | --- | --- | --- | .5 | .2 | .3 | 1.1 | .4 | .2 | .2 | 1.1 |
| Mn, ppm (mg/l) | .1 | .1 | .0 | .2 | .0 | .02 | .0 | .1 | .0 | .05 | .0 | .2 |
| Sr, ppm [1] | .063 | .014 | .039 | .088 | | | | | | | | |
| Discharge, cfs [7] | 21,420 | 8,188 | 13,490 | 40,790 | 31,340 | 14,290 | 18,870 | 66,450 | 38,880 | 17,400 | 22,600 | 76,820 |

[1] Chemical analyses of filtered samples for Sr by ORNL. All other chemical analyses are of raw samples by Tennessee Stream Pollution Control Board.
[2] Sampling period, August 1960 through November 1962. Samples were not discharge weighted.
[3] Sampling period, December 1960 through November 1962. Samples were discharge weighted.
[4] Standard deviation of 30-day composite samples from mean for sampling period.
[5] Not calculated.
[6] Dash indicates that constituent was not determined.
[7] Not discharge weighted. Discharge data is time weighted.

by centrifugation prior to analysis. The suspended solids content, turbidity, and color of Tennessee River water varied directly with discharge, but this pattern was not well defined in Clinch River water. At two stations, strontium showed a significant positive correlation with calcium, as one might expect if the two chemically similar elements were both derived from natural weathering processes. In the lower Clinch River, stable strontium varied inversely with suspended sediment, possibly as a result of dilution of the river water by low-strontium surface runoff at times of high rainfall.

Each of the major chemical constituents of Whiteoak Creek water—bicarbonate, calcium, sulfate, sodium, magnesium, and chloride—showed a significant positive correlation with each of the other major constituents and with specific conductance. All but sulfate showed significant negative correlations with discharge as a result of dilution of Whiteoak Creek water by surface runoff at times of high rainfall. Most of the sodium, chloride, sulfate, and nitrate in Whiteoak Creek water at Whiteoak Dam probably originated in waste from ORNL.

Statistical tests indicated that for sampling stations on the same stream, means and variances for 30-day composite samples were the same within statistical limits for most of the individual chemical constituents. When mean concentrations for 7-day composites were compared for a 24-week period during the winter and spring of 1960–61, high positive correlations were ob-

tained between the pair of stations at CRM 41.5 and CRM 5.5, and between the pair of stations at TRM 529.9 and TRM 471.0 for constituents related to surface runoff and thus more variable in relation to location on the river—that is, turbidity, apparent color, centrifuged color, iron, and manganese. These results suggest that one sampling station on each river would have been sufficient to characterize the contents of chemical constituents not directly related to solids suspended in the water when the comparison was based on 30-day composite samples. They also emphasize the lack of major change in chemical composition of either the Clinch River or the Tennessee River as a result of the entry of tributary streams in the reaches of river studied.

## RADIOCHEMICAL COMPOSITION OF WATER

The results of radiochemical analyses of discharge-weighted 7-day composite water samples collected at Whiteoak Dam (WOCM 0.6) during the 2-year sampling period have been reported by Churchill and others (1965). Mean and median values for the sampling period, beginning November 1960 and ending November 1962, for the distribution of the four most important radionuclides between suspended solids (particles greater than 0.7 micron) and the water phase (dissolved or as particles less than 0.7 micron) are listed in table 6. It is apparent that most of the cesium-137 is associated with suspended solids having a diameter

larger than that of colloidal particles. The other three radionuclides occur mainly either in solution or in association with suspended solids of colloidal or near-colloidal size.

The distribution of the four radionuclides between suspended solids and the water phase in 7-day composite samples from five of the six water-sampling stations on the Clinch River and the Tennessee River also is shown in table 6. Most of the cesium-137 in Clinch River water is associated with suspended solids larger than 0.7 micron in diameter, but this apparently is not true in the Tennessee River. However, much of the cesium-137 in Tennessee River water may be associated with finer particles that remained with the water phase during processing of the samples. The cesium-137 content of bottom sediment in the lower Clinch River, and in the Tennessee River between the mouth of the Clinch River and Watts Bar Dam (TRM 471.0), is primarily due to deposition of the larger, settleable particles of suspended sediment.

The radionuclides cobalt-60, ruthenium-106, and strontium-90 are associated primarily with the water phase of the two rivers, but the significant fractions of cobalt-60 and ruthenium-106 that are associated with suspended solids in the lower Clinch River (table 6) may be taken as evidence that there is some association of those two radionuclides with suspended fine particles in both rivers. The presence of all four radionuclides in Clinch River bottom sediment (Carrigan, 1969; Pickering, 1969) further indicates their affinity for solids carried by the river water.

The content of cobalt-60 showed a high positive correlation with that of ruthenium-106 in 7-day composite water samples taken at Whiteoak Dam (coefficient of correlation 0.93) and the two downstream sampling stations on the Clinch River (0.71 at CRM 14.4; 0.74 at CRM 5.5) during the two sampling periods. This correlation probably resulted from the common origin of the two radionuclides in seepage from liquid-waste disposal pits in Whiteoak Creek basin (Lomenick and Gardiner, 1965). No significant radionuclide correla-

tions were observed in samples from the Tennessee River, possibly because concentrations of cesium-137 and cobalt-60 were near the lower limit of detection in many of the samples and could not be determined accurately.

## RELATIONSHIPS BETWEEN STABLE CHEMICAL COMPOSITION AND RADIONUCLIDE CONTENT OF THE STREAMS

Comparisons between variations in radionuclide content and variations in stable chemical content of water samples from the individual stations have provided some evidence concerning the origin and the chemical form of the various radionuclides in the water. A high positive correlation of the content of strontium-90 with pH (coefficient of correlation 0.82) in weekly samples of water passing Whiteoak Dam (WOCM 0.6) suggests that much of the strontium-90 in Whiteoak Lake may be associated with precipitated calcium carbonate. High positive correlations of ruthenium-106 and cobalt-60 with the nitrate content of water passing Whiteoak Dam (0.75 and 0.80 respectively), together with their very high mutual correlation (0.93), confirms previous observations (Morton, 1963, p. 19) that the source of the two radionuclides is high-nitrate seepage water from intermediate-level waste-disposal pits located in the basin of Whiteoak Creek.

A high positive correlation of cesium-137 content with specific conductance (0.81), and with several of the minor chemical constituents in Whiteoak Creek water, and its lack of significant correlation with the contents of ruthenium-106, cobalt-60, and nitrate, suggests that the origin of cesium-137 is not the same as that of the other two radionuclides, and supports the contention (Struxness and others, 1967, p. 27) that treated process waste water released from ORNL, and erosion of sediment from former impoundments in Whiteoak Creek, are the major sources of cesium-137 in the creek water. Concentrations of suspended solids in water samples from Whiteoak Creek were not determined, but it can be assumed, on the basis of the distri-

TABLE 6.—*Radionuclide distribution between suspended solids and water phase at six water-sampling stations* [1]

| Station location | Strontium-90 | | | | Cesium-137 | | | | Cobalt-60 | | | | Ruthenium-106 | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Percent in suspended solids | | Percent in dissolved solids | | Percent in suspended solids | | Percent in dissolved solids [2] | | Percent in suspended solids | | Percent in dissolved solids [2] | | Percent in suspended solids | | Percent in dissolved solids [2] | |
| | Mean | Median | Mean | Median | Mean | Median | Mean | Median | Mean | Median | Mean | Median | Mean | Median | Mean | Median |
| CRM 41.5 | 24 | 21 | 76 | 79 | 82 | 100 | 18 | 0 | 5 | 0 | 95 | 100 | 44 | 29 | 56 | 71 |
| WOCM 0.6 | 2 | 1 | 98 | 99 | 69 | 79 | 31 | 21 | 19 | 12 | 81 | 88 | 6 | 4 | 94 | 96 |
| CRM 14.4 [3] | 6 | 4 | 94 | 96 | 92 | 100 | 8 | 0 | 27 | 25 | 73 | 75 | 21 | 17 | 79 | 83 |
| CRM 5.5 | 9 | 6 | 91 | 94 | 86 | 100 | 14 | 0 | 30 | 25 | 70 | 75 | 21 | 16 | 79 | 84 |
| TRM 529.9 | 9 | 6 | 91 | 94 | 30 | 0 | 70 | 100 | 2 | 0 | 98 | 100 | 11 | 7 | 89 | 93 |
| TRM 471.0 | 10 | 6 | 90 | 94 | 19 | 0 | 81 | 100 | 3 | 0 | 97 | 100 | 15 | 8 | 85 | 92 |

[1] Data from Churchill and others, 1965.
[2] Includes suspended solids less than 0.7 micron in diameter.
[3] Sampling period, January 1962 through November 1962. For all other stations, sampling period was November 1960 through November 1962.

bution of cesium-137 between suspended and dissolved solids in the samples on which radiochemical analyses were performed (Churchill and others, 1965) and studies of suspended sediment in Whiteoak Creek above Whiteoak Lake (Morton, 1963, p. 28), that a high positive correlation between the concentration of cesium-137 and the content of suspended solids in water samples collected at Whiteoak Dam would have been observed if the appropriate determinations had been made.

No significant correlations were observed between radionuclide and stable chemical concentrations for 7-day composite water samples from CRM 14.4, but for 30-day composite samples, strontium-90 and ruthenium-106 correlated positively with iron (0.90 and 0.85 respectively) and negatively with stable strontium (−0.94 and −0.78 respectively). This correlation suggests that the two radionuclides may be in some way related to surface runoff. It should be noted that both stable chemical analyses and radiochemical analyses of samples collected at this station were performed on the supernatant liquid remaining after centrifugation of the samples to remove large-diameter particles of suspended sediment.

At CRM 5.5, concentrations of cesium-137 showed significant positive correlations with the contents of suspended solids, iron, and manganese (coefficients of correlation 0.63, 0.65, and 0.56 respectively), and with turbidity and apparent color (0.62 and 0.57 respectively), components known to vary with the amount of suspended sediment contributed to the river by surface runoff. A better correlation would not be expected because of the many sources of suspended sediment entering the Clinch River and the commonly uneven short-term distribution of rainfall in the basin.

No high correlations of radiochemical constituents with stable chemical constituents were observed for samples obtained at the three sampling stations on the Tennessee River, but some weak correlations suggested that the content of ruthenium-106 in the water was higher when suspended sediment contributed by surface runoff was most abundant, and it was lower when the dissolved-solids concentration was high.

It should be noted that correlation of the content of certain radionuclides with parameters related to the suspended-solids content of water in the Clinch River and Whiteoak Creek do not necessarily indicate that the radionuclides are associated with suspended solids in the two streams. Flushing out of seeps from waste-disposal pits in the basin of Whiteoak Creek during the initial period of rainfall would produce an increased content of ruthenium-106 and cobalt-60 in Whiteoak Creek water at the same time that turbulence due to runoff was producing an increase in suspended solids in the

stream. Supporting evidence, such as that given in table 6, must therefore be sought when a relationship of this sort is suspected.

## CONCLUSIONS

Comprehensive chemical analyses of composite water samples collected from Whiteoak Creek, the Clinch River, and the Tennessee River over a 3-year period indicated that all three streams contain water of the calcium bicarbonate type, presumably as a result of the abundance of limestone and dolomite bedrock underlying their drainage basins. Tennessee River water is similar in composition to Clinch River water, but contains somewhat less bicarbonate, calcium, magnesium, and suspended and dissolved solids, and somewhat more sodium and chloride. Whiteoak Creek water is more highly mineralized than the other two streams, and has a higher average content of sulfate, nitrate, phosphorus, and sodium.

Turbidity, apparent color, centrifuged color, and suspended solids increased seasonally with increased amounts of rainfall and runoff in the Clinch and Tennessee Rivers, and the contents of major dissolved constituents and total dissolved solids in the two rivers increased during the autumn when contribution of ground water to streamflow is greatest and dilution of wastes is least. Iron and manganese appeared to be present in the two streams predominantly in association with suspended solids. The composition of water in Whiteoak Creek showed less seasonal variation than water in the other two streams because of the substantial contribution to its total flow of treated process waste water from Oak Ridge National Laboratory.

In the Clinch and Tennessee Rivers, progressive changes in chemical composition of the water with distance downstream in the two study reaches were small for most of the major chemical constituents. However, changes with distance downstream in turbidity, color, suspended solids, iron content, and manganese content were observed during rainy periods when the streams were receiving a heavy contribution of overland runoff.

Most of the cesium-137 released from Whiteoak Creek was associated with suspended solids. Correlation of cesium-137 with other constituents associated with suspended sediment in the Clinch River indicated that this association persisted during downstream transport of the radionuclide. A high positive correlation of strontium-90 with pH at Whiteoak Dam (WOCM 0.6) may have been the result of association of strontium-90 with precipitated calcium carbonate in Whiteoak Lake, as suggested by other investigators.

Close similarities in variations in concentration between ruthenium-106 and cobalt-60 in both Whiteoak Creek and the Clinch River, and a positive correlation

of the two radionuclides with nitrate at Whiteoak Dam, reflected their common origin in high-nitrate solutions released to liquid-waste disposal pits in the basin of Whiteoak Creek. Their lack of significant correlation with cesium-137 or strontium-90 indicated other origins for those radionuclides.

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